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Process for the preparation of trihydrocarbylsilylated carboxylate monomers.

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Field of the invention

The invention relates to a new method for the preparation of trihydrocarbylsilylated carboxylate monomers

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Background of the invention

Antifouling paints are used to prevent and delay the fouling of underwater structures (e.g. ships' bottom, docks, fishnets, and buoys) by various marine organisms such as shells, seaweed, and aquatic bacteria. When such marine organisms adhere and propagate on an underwater structure like the bottom of a ship, the surface roughness of the whole ship may be increased to the point of inducing a decrease of velocity of the ship or an increase of fuel consumption. Further, removal of such aquatic organisms from the ship's bottom needs much labour and a long period of working time in a costly dry dock. In addition, if these organisms adhere and propagate on an underwater structure such as a steel structure, they deteriorate the anticorrosive coating films leading to a reducing of the lifetime of the underwater structure.

Underwater structures are therefore coated with antifouling paint employing polymers containing various hydrolysable groups and more specifically organosilyl groups.

Amongst those antifouling paints is for example, an antifouling paint of the hydrolysable self-polishing type proposed in WO 84/02915 and JP 63215780 A, which employs a (meth)acrylic ester polymer having triorganosilyl groups in the side chains. Other examples of patents and patent applications related to the use of organosilyl acrylate polymers in antifouling compositions are EP

131626, US 4593055, US 4594365, JP 63118381 A, EP 0775733, WO 96/38508, EP 802243, EP 0714957, JP 07018216 A, JP 01132668 A, JP 05077712 A, JP 01146969 A and US 4957989, which are hereby incorporated by reference.

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Some of the polymers used in the above-described antifouling paints are based on silylated carboxylate monomers.

Several processes are known for the synthesis of silylated carboxylate monomers.

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JP 5306290 A discloses a process to obtain a methacrylic functional group-containing organosilicon compound. The process comprises reacting methacrylic acid with a halogenoalkylsilane (e.g. trialkylsilylchloride) in the presence of a tertiary amine compound having a cyclic structure. This process has disadvantages such as the reduced availability and storage stability of the silyl chloride. Moreover, the reaction yields as a by-product a hydrogen halide (which provokes the corrosion of the production equipment) or a halide salt (which has to be removed by filtration).

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A synthesis of trimethylsilyl methacrylate from methacrylic acid and hexamethyldisilazane is described by A.Chapman & A.D.Jenkins in J.Polym.Sci. Polym.Chem.Edn. vol 15, p.3075 (1977).

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JP 10195084 A discloses the reaction of unsaturated carboxylic acids such as acrylic acid or methacrylic acid with a trialkylsilylhydride compound in the presence of a copper catalyst. One of the disadvantages of this method is the risk of hydrogenation of the unsaturated carboxylic anhydride due to a side reaction of the produced H₂ on the carbon-carbon double bond.

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J.Valade describes in "Compte Rendu de l'Académie des Sciences" n° 246, p. 952-953 (1958) the reaction of hexamethyldisiloxane or hexaethyldisiloxane

with acetic anhydride or benzoic anhydride in the presence of zinc chloride whereas maleic anhydride or succinic anhydride do not react with hexamethyldisiloxane or hexaethyldisiloxane in the presence of zinc chloride.

5 Therefore, an object of the present invention is to provide a novel process capable of readily preparing trihydrocarbylsilylated unsaturated carboxylate monomers in a high yield.

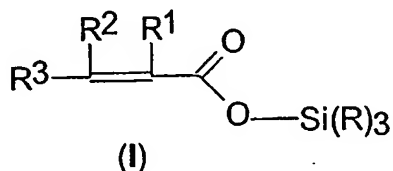
Another object of the present invention is to provide a novel process preparing said monomers from easily available starting materials.

10 A further object of the present invention is to provide a novel process offering an improvement vis-à-vis of the disadvantages disclosed above.

The present invention is based on the reaction of either linear or cyclic unsaturated carboxylic anhydrides with hexahydrocarbyldisiloxane to
15 synthesise, in the presence of a catalyst, trihydrocarbylsilylated unsaturated carboxylate monomers.

Summary of the invention

The present invention relates to a new process for the preparation of
20 trihydrocarbylsilylated unsaturated carboxylate monomers of either general formula (I)



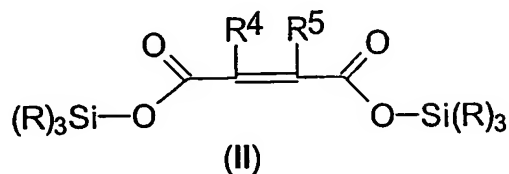
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wherein

each R independently represents an alkyl, a substituted alkyl, an aryl or a substituted aryl group, R¹, R² each independently represents a hydrogen atom
30 or an alkyl or substituted alkyl group, an aryl or a substituted aryl group, R³

represents a hydrogen atom, an alkyl or substituted alkyl group, an aryl or a substituted aryl group or $-\text{COOR}^6$ wherein R^6 represents an alkyl, a substituted alkyl, an aryl or a substituted aryl group,

5 or general formula (II)

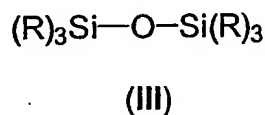


10 wherein

each R is as already defined above

R^4 , R^5 each independently represents a hydrogen atom or an alkyl or substituted alkyl group, an aryl or substituted aryl group

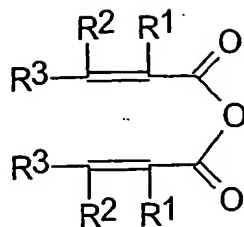
15 which process comprises the step of reacting, in the presence of a catalyst, a hexahydrocarbyldisiloxane of formula (III)



20 wherein

R is as already defined above

either with an unsaturated carboxylic anhydride of formula (IV),



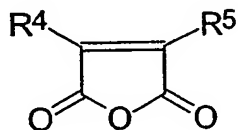
(IV)

5 wherein

R¹, R², R³ are as already defined above

or with an unsaturated carboxylic anhydride of formula (V)

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(V)

wherein R⁴, R⁵ are as already defined above.

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Preferably, the catalyst used in the present invention consists of a mixture of a strong acid and a nucleophilic base.

(For the purposes of clarity general formula (II) has been depicted separately
 20 but may also be considered as an alternative of formula (I) wherein R⁶
 represents -Si(R)₃ with R as already defined above).

The term "alkyl", as used herein unless otherwise defined, relates to saturated hydrocarbon radicals having straight, branched, cyclic or polycyclic moieties or
 25 combinations thereof and contains 1 to 20 carbon atoms, preferably 1 to 10

- carbon atoms, more preferably 1 to 8 carbon atoms, still more preferably 1 to 6 carbon atoms, yet more preferably 1 to 4 carbon atoms. Said radical may be a substituted alkyl group, i.e. optionally substituted with one or more substituents independently selected from alkyl, aryl, alkoxy, halogen, hydroxy or amino radicals. Examples of such alkyl radicals may be independently selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, 2-methylbutyl, 2,3-dimethylbutyl, lauryl, pentyl, iso-amyl, n-amyl, n-hexyl, cyclohexyl, 3-methylpentyl, n-octyl, t-octyl, n-dodecyl and the like.
- 10 In a preferred embodiment R, R¹, R², R³, R⁴, R⁵ and R⁶ each independently represent a linear, branched, or cyclic or polycyclic alkyl, substituted alkyl, aryl or substituted aryl group, saturated or unsaturated, containing from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms, yet more preferably R is 4 carbon atoms. Preferably, R is
- 15 chosen from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, sec-butyl, t-butyl, 2-methylbutyl, 2,3-dimethylbutyl, lauryl, pentyl, n-amyl, iso-amyl, n-hexyl, cyclohexyl, 3-methylpentyl, n-octyl, t-octyl, n-dodecyl, phenyl or substituted phenyl, and the like. More preferably, R is chosen from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, sec-
- 20 butyl, t-butyl, 2,3-dimethylbutyl, n-amyl, n-hexyl, n-octyl, t-octyl, n-dodecyl, lauryl, phenyl or substituted phenyl wherein the substituents may be linear or branched alkyl, aryl, halogene, alkoxy, phenoxy or nitro. Yet in a more preferred embodiment R is n-butyl, or isopropyl.
- 25 In a preferred embodiment R¹, R², R³, R⁴ and R⁵ each independently represent hydrogen atom or a methyl group.

The term "aryl" as used herein, relates to an organic radical derived from an aromatic hydrocarbon by removal of one hydrogen, and includes any

30 monocyclic, bicyclic or polycyclic carbon ring of up to 7 members in each ring, wherein at least one ring is aromatic. Said radical may be a substituted aryl group ie optionally substituted with one or more substituents independently

selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of aryl includes phenyl, p-methylphenyl, stearyl, phenethyl, (2-methyl)-phenethyl, 4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, 4-acetamidophenyl, 2-methyl-3-acetamidophenyl, 2-methyl-3-aminophenyl, 3-methyl-4-aminophenyl, 2-amino-3-methylphenyl, 2,4-dimethyl-3-aminophenyl, 4-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, 1-naphthyl, 2-naphthyl, 3-amino-1-naphthyl, 2-methyl-3-amino-1-naphthyl, 6-amino-2-naphthyl, 4,6-dimethoxy-2-naphthyl, tetrahydronaphthyl, indanyl, biphenyl, phenanthryl, anthryl or acenaphthyl and the like.

As used herein, the term "independently" indicates that each radical R so described, can be identical or different.

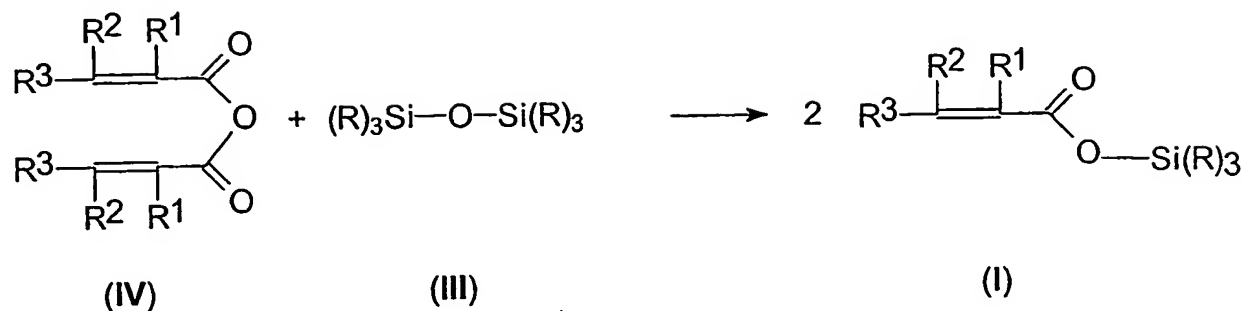
In the embodiment when R^3 is $-\text{COOR}^6$, the trihydrocarbylsilylated unsaturated carboxylates of general formula (I) and the unsaturated carboxylic compound (IV) can be of either cis (maleic) or trans (fumaric) configuration.

In a more preferred embodiment the trihydrocarbylsilylated unsaturated carboxylates obtained by the process of the invention are trihydrocarbylsilyl acrylates or trihydrocarbylsilyl methacrylates.

The present invention will be further disclosed in detail hereunder.

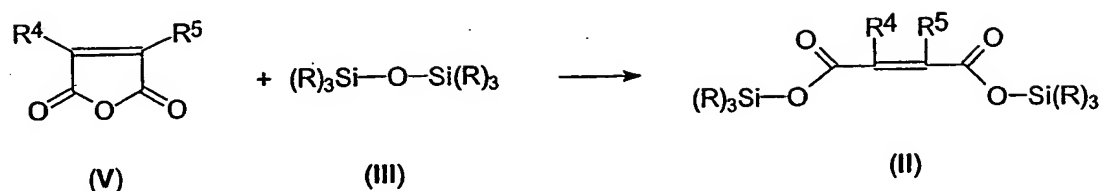
Detailed description of the invention

The present invention relates to a new process for the synthesis of trihydrocarbylsilylated unsaturated carboxylates according either to the general scheme 1:



or to the general scheme 2 :

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Unsaturated carboxylic anhydride represented by the above formula (IV) or (V) is mixed with hexahydrocarbyldisiloxane of formula (III) with or without solvent. Examples of solvents, which can be used in the process according to the invention, include hexane, cyclohexane, toluene, xylene, pentane, heptane, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthalene, diethylether, diisopropyl ether, diisobutyl ether, THF, Dioxane, dichloromethane or mixtures thereof. Preferably, an inert solvent is used, more preferably, a hydrocarbon inert solvent such as hexane, cyclohexane, toluene or xylene.

The reaction may be conducted with an added polymerisation inhibitor. Preferably, a radical polymerisation inhibitor is used. A suitable polymerisation inhibitor is o-methoxyphenol. The reaction progress may be monitored by any suitable analytical method.

Preferably, the solvent is at least 10 wt% of the total reaction mix at the start of the reaction, more preferably, at least 20 wt%, most preferably, at least 30 wt%. The reaction may also be without solvent and accordingly suitable

ranges of solvent are 0-99 wt% of the total reaction mix, more preferably, 20-80 wt%, most preferably 30-70 wt%.

5 Examples of unsaturated carboxylic anhydrides, which can be used in the process according to the invention include acrylic anhydride, methacrylic anhydride, crotonic anhydride, angelic anhydride, tiglic anhydride, maleic anhydride, citraconic anhydride (methylmaleic anhydride).

10 Examples of the trihydrocarbylsilylated unsaturated carboxylate monomers prepared by the process of the invention using (meth)acrylic anhydride include trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate, triisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-s-butylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-
15 n-dodecylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, tri t-butylsilyl (meth)acrylate.

Other examples include ethyldimethylsilyl methacrylate, n-butyldimethylsilyl
20 methacrylate, bis(trimethylsilyl) itaconate, t-butyl dimethylsilyl (meth)acrylate, diisopropyl-n-butylsilyl (meth)acrylate, n-octyldi-n-butylsilyl (meth)acrylate, diisopropylstearyl silyl (meth)acrylate, dicyclohexylphenylsilyl (meth)acrylate, t-butyl diphenylsilyl (meth)acrylate, phenyldimethylsilyl (meth)acrylate, n-hexyldimethylsilyl (meth)acrylate, tert-octyldimethylsilyl (meth)acrylate,
25 phenethyldimethylsilyl (meth)acrylate, (2-methyl)-phenethyldimethylsilyl (meth)acrylate, (2,3-dimethylbutyl)dimethylsilyl (meth)acrylate, cyclohexyldimethylsilyl (meth)acrylate and lauryldiphenylsilyl (meth)acrylate.

30 Examples of the trihydrocarbylsilylated unsaturated carboxylate monomers prepared by the process of the invention using maleic anhydride include bis triisopropylsilyl maleate, bis tri-n-butylsilyl maleate, bis t-butyldiphenylsilyl

maleate, bis t-butyldiphenylsilyl maleate or the corresponding fumarate isomers.

The reaction is conducted in the presence of a catalyst comprising of, more preferably consisting of, a mixture of a strong acid and a nucleophilic base. By "strong acid", we mean an acid having a pKa value preferably less than 5, more preferably less than 2, and most preferably less than -5. Preferably, the "strong acid" is stronger than acetic acid, more preferably stronger than chloroacetic acid, most preferably, stronger than trichloroacetic acid. By "nucleophilic base", we mean a base having an available electron pair for donation. More specifically, by 'nucleophilic base', we mean an organic Lewis base having an electron pair available for interacting in a reversible manner with the acylation agent, more preferably the base is a nitrogen containing molecule which is more basic than triethylamine, more preferably this amine is a heteroaromatic amine, more preferably an heteroaromatic mono or polyamine substituted or not with one or more amino groups, more preferably an heteroaromatic mono or polyamine substituted or not with one or more amino groups in which at least one of the nitrogen electron pairs is conjugated with the aromatic ring in such a manner that it brings an increase in negative charge on another amino function of the molecule.

Among strong acids that can be used, one can cite sulfuric acid, phosphoric acid, chlorhydric acid, bromhydric acid, hydriodic acid, nitric acid, trifluoromethanesulfonic acid or perfluoroalkylsulfonic acids, methanesulfonic acid, para-toluene sulfonic acid, trifluoroacetic acid. A preferred strong acid is trifluoromethanesulphonic acid. Strong ion exchange resins (sulfonated styrene copolymers) such as Amberlyst® 15 resin (CAS RN = 39389-20-3) or perfluoroalkylsulfonic resins such as Nafion® NR50 resin (CAS RN = 118473-68-0) may also be used. Among nucleophilic bases that can be used, one can cite pyridine, 2- (dimethylamino)pyridine, 4-(dimethylamino)pyridine, 4-piperidino pyridine, 4-(4-methylpiperidino)pyridine, 4-pyrrolidinopyridine, 4-morpholinopyridine, imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, polymer- bound dimethylaminopyridine (examples of which

may be found in US 4997944 incorporated herein by reference), 1-methylbenzimidazole, 2-methylbenzimidazole, benzimidazole and, in addition, N-methyl imidazole(NMI), N,N-dimethylamino pyridine(DMAP), hexamethylphosphoric triamide(HMPA), 4,4 dimethyl imidazole, N-methyl-2-pyridone(NMP), pyridine N-oxide, triphenylphosphine oxide, tributyl phosphine,
5 2,4 dimethyl pyridine, N-methyl-4-pyridone, ZnCl₂, 3,5 dimethyl pyridine, imidazole, trimethylamine, triethylamine, p-dimethylaminobenzaldehyde, 1,2-dimethyl imidazole, and montmorillonites such as K10 or KSF.

10 Preferred nucleophilic bases include 2- (dimethylamino)pyridine, 4-(dimethylamino)pyridine, 4-(4-methylpiperidino)pyridine, 4-pyrrolidinopyridine, imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, polymer-bound dimethylaminopyridine, 1-methylbenzimidazole, 2-methylbenzimidazole, benzimidazole. A more preferred nucleophilic base is 4-(dimethylamino)
15 pyridine or derivatives thereof.

Preferably, the catalyst is present at a level of 0.2-40 mol % (mol/mol siloxane), more preferably 1-24 mol %, most preferably 2-10 mol % in the reaction medium at the start of the reaction. In a batch process, the catalyst
20 level relative to moles of siloxane in the starting reaction medium will increase during the reaction, whereas in a continuous process the catalyst level will remain relatively constant throughout the process except towards the end of any such process when it may rise relative to the level of siloxane as feed reactants are no longer added to the process.

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Preferably the molar ratio of strong acid to nucleophilic base in the catalyst is in the range 1:10 to 10:1, more preferably, 1:5 to 5:1, most preferably 1:2 to 2:1. Especially preferred is a range between 3:2 to 2:3, more especially preferred is a ratio of approximately 1:1.

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The reaction is preferably carried out at a temperature between 30°C and 130°C, more preferably between 40°C and 120°C, and most preferably between 50°C and 100°C, for example at 60°C or 90°C.

- 5 Preferably, the reaction takes place in less than 24 hours, more preferably, less than 20 hours, more preferably less than 12 hours.

Preferably, the polymerisation inhibitor is present in the range 0.001-10% wt/wt of the total reaction mix, more preferably 0.001-5% wt/wt and most preferably
10 0.01-2% wt/wt.

Preferably, the molar ratio of siloxane:anhydride is between 1:100 and 50:1, more preferably between 10:1 and 1:10, most preferably, between 2:1 and 1:2. Preferably, the molar ratio of siloxane:anhydride is approximately 1:1.

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The reaction may be carried out at any convenient pressure, for instance atmospheric pressure.

The advantage of this invention is that the process uses reactants, which can
20 be easily handled. Hexahydrocarbyl disiloxanes may be considered as easily accessible since they are formed as a by-product during acidic deprotection of silyl protected reactive functional groups such as e.g. alcohols, amines or carboxylic acids (as described in "Protective Groups in Organic Synthesis" T.W.Greene and P.G.M.Wuts J.Wiley & Sons, 1999).

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Another advantage lies in the simplicity and safety of the procedure (no by-products, hence no trapping of corrosive gaseous matter).

Due to its one step process, the present invention is a substantial improvement
30 over the existing methods.

Moreover, due to the possibility of using numerous hexahydrocarbyldisiloxanes as reactants leading to the production of a wide range of trihydrocarbylsilylated unsaturated carboxylate monomers, the process of the present invention is a substantial improvement over the existing methods.

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The trihydrocarbylsilylated unsaturated carboxylate monomers obtained by the process of the invention can be polymerised with various other monomers such as vinyl monomers including acrylic esters, methacrylic esters, styrene, vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate), vinyltoluene, alpha-methylstyrene, crotonic esters, and itaconic esters.

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The polymers and copolymers of said monomers are useful in coating or paint composition. More preferably they are used in antifouling coating or paint compositions.

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The antifouling coating compositions prepared using the monomers obtained by the process of the invention are tin-free coatings and provide an alternative to the present self-polishing coating technology based on hydrolysable tributyltin polymers (the use of which is due to be banned in antifouling paints by 2003). The trihydrocarbylsilylated unsaturated carboxylate monomers provided by the process of the invention compared to organotin monomers are less toxic, less polar, more hydrophobic and more stable.

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The invention will now be described by way of illustration only and with reference to the accompanying examples.

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Examples and comparative examples

All the monomers used in the examples and comparative examples are purchased from Aldrich and used without any preliminary purification.

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In examples 1 and 2, NMR datas have been determined in CDCl_3 and are expressed as delta versus TMS.

Example 1 (according to the invention)

- 5 285 mg of 4-(dimethylamino)pyridine and 352 mg of trifluoromethanesulfonic acid were successively added, at room temperature, to a mixture of 3.8g of hexamethyldisiloxane and 3.6g of methacrylic anhydride. The solution heated at 60°C for 16h to furnish trimethylsilyl methacrylate.

Trimethylsilyl methacrylate: ^{13}C NMR : 167.7, 137.6, 127.1, 18.2, -0.257 ; ^{29}Si NMR : 24.3; IR (film): 2963, 1703, 1335, 1256, 1178, 874, 854 cm^{-1} .

10

Example 2 (according to the invention)

- 146 mg of 4-(dimethylamino)pyridine and 180 mg of trifluoromethanesulfonic acid were successively added, at room temperature, to a mixture of 5g of hexabutyldisiloxane and 1.8g of methacrylic anhydride. The solution was heated at 60°C for 16h to furnish tributylsilyl methacrylate.
- 15

Tri-n-butylsilyl methacrylate: ^{13}C NMR : 167.8, 137.9, 126.0, 26.7, 25.5, 18.5, 13.5, 14.0; ^{29}Si NMR : 23.1; IR (film): 2959, 2927, 1703, 1334, 1174, 886, 766 cm^{-1} .

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Example 3 (according to the invention)

- 185 mg of 4-(dimethylamino)pyridine and 228 mg of trifluoromethanesulfonic acid were successively added, at room temperature, to a mixture of 5 g of hexaisopropyldisiloxane and 2.33 g of methacrylic anhydride. The solution was heated at 90°C for 24 h to furnish triisopropylsilyl methacrylate
- 25

Triisopropylsilyl methacrylate: ^{13}C NMR: 167.7, 138.0, 126.2, 18.8, 18.1, 2.4; ^{29}Si NMR: 21.8; IR (film): 2949, 2870, 1703, 1334, 1178, 884, 751 cm^{-1} .

Comparative example 1 (according to J.Valade in Compte Rendu de l'Académie des Sciences n° 246, p. 952-953 (1958))

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8.4 g of zinc chloride were added, at room temperature, to a mixture of 5 g of hexamethyldisiloxane and 6.25 g of methacrylic anhydride. The solution was heated at 110°C. After 16h no transformation was observed.

5 Comparative example 2: (catalyst is strong acid only)

352 mg of trifluoromethanesulfonic acid were added, at room temperature, to a mixture of 5 g of hexamethyldisiloxane and 6.25 g of methacrylic anhydride. The solution was heated at 60°C. After 16h no transformation was observed.

10 Comparative example 3: (catalyst is nucleophilic base only)

285 mg of 4-(dimethylamino)pyridine were added, at room temperature to a mixture of 5g of hexamethyldisiloxane and 6.25 g of methacrylic anhydride. The solution was heated at 60°C. After 16h no transformation was observed.

15 Comparative example 4: (catalyst is strong acid and weak nucleophilic base)

185 mg of pyridine and 352 mg of trifluoromethanesulfonic acid was added, at room temperature, to a mixture of 3.8 g of hexamethyldisiloxane and 3.6 g of methacrylic anhydride. The solution was heated at 60°C. After 16h no transformation was observed.

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The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by

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reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except
30 combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is
5 one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims,
10 abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.